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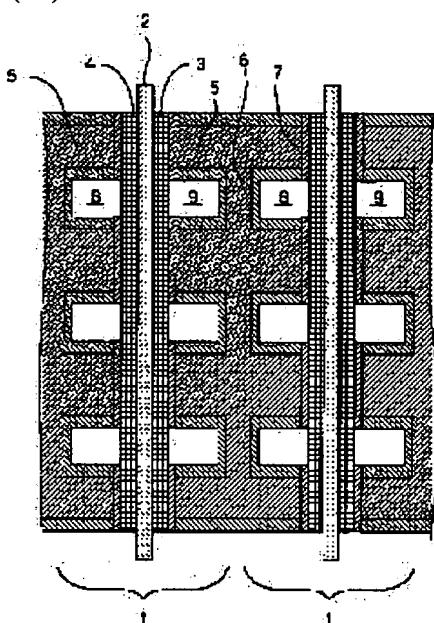
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(54) SEPARATOR FOR FUEL CELL



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a separator for a fuel cell made from aluminium which has an outstanding corrosion resistance.

SOLUTION: The separator for the fuel cell consists of an aluminium metal plate, and has a contact surface with an electrode or an electricity collector body and a reaction gas aeration slot, and an alumite coat film is formed on the surface of the reaction gas aeration slot.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the separator used for a fuel cell, especially the mounted fuel cell for power of an automobile.

[0002]

[Description of the Prior Art] The energy conversion efficiency of a fuel cell from a fuel to the electrical and electric equipment is high, and it attracts attention as a next-generation power plant in order not to discharge harmful matter. Especially the macromolecule ion-exchange-membrane mold fuel cell that operates in a temperature field 150 degrees C or less is studied briskly, and utilization several years after is expected. This fuel cell can operate at comparatively low temperature, its output density of a generation of electrical energy is high, and since it can miniaturize, it is suitable as a fuel cell home use and for mount.

[0003] Usually, a macromolecule ion-exchange-membrane mold fuel cell fixes a fuel electrode and an oxygen electrode (air electrode) to both sides of a solid-electrolyte membrane, forms a cell (cel), and is constituted by carrying out a laminating through the tabular separator which prepared the aeration slot which supplies fuel gas and air for this. The fluororesin system ion exchange membrane which has a sulfonic group as a solid-electrolyte membrane is used, and an electrode is formed by what distributed Repellent PTFE and the noble-metals particle catalyst to carbon black. In case a hydrogen-oxygen fuel cell operates, the proton which hydrogen gas oxidized and was produced advances into an electrolyte, combines with a water molecule, becomes H_3O^+ , and moves to a positive-electrode side. In a positive-electrode side, the oxygen introduced from the aeration slot obtains the electron generated by oxidation reaction of hydrogen, combines with the proton in an electrolyte, and serves as water. Electrical energy can be continuously taken out by continuing these reaction processes. Although the theoretical electromotive force of this cell is 1.2V, it is the causes, such as a voltage drop by the contact resistance of polarization of an electrode, the crossover (phenomenon in which fuel gas penetrates an electrolyte and leaks to an air electrode) of reactant gas, an electrode, and a charge collector, actually, and output voltage is about 0.6-0.8V. Therefore, in order to obtain a practical output, it is necessary to carry out the stack of dozens of cells through a separator, and to connect in serial.

[0004] Since H^+ exists so much in an electrolyte so that the above-mentioned generation-of-electrical-energy principle may show, water or a steam serves as [near / which exist so much / the interior of an electrolyte, and near the electrode] strong acid nature. Moreover, although oxygen combines with H^+ by the positive-electrode side and water is generated, a hydrogen peroxide may generate depending on the operating state of a cell. Since a separator is built into the bottom of such an environment, in addition to electrical conductivity and airtightness, it is

required that it should have high chemistry and electrochemical stability (corrosion resistance). [0005] Many of conventional separators for fuel cells machine a graphite plate. Mechanical strength is low and a graphite separator has high processing cost, while electric resistance is low and corrosion resistance is high. It is difficult to apply the present graphite separator to the fuel cell for mount as it is, since for the separator used for the fuel cell for mount to have high mechanical strength, and to be able to process it by low cost is demanded. Although the method of manufacturing a separator by mixing with resin, injection molding graphite powder, and carrying out elevated-temperature baking further in recent years is examined, since the consistency of the baking object acquired is low, there is a problem that airtightness is bad. A production process becomes complicated although it is possible to raise a consistency by being immersed and carbonization re-calcinating this separator by resin. In addition, the contact electricity resistance of the separator manufactured in this way is several times as strong as the conventional graphite separator, and output voltage lowering of a cell is not avoided.

[0006] The separator which consists of a metal in addition to a graphite separator is also examined. Bulk electric resistance is low, a metal separator has high airtightness and high mechanical strength, and reduction of processing cost is easy for it. Moreover, since thickness of a separator can be made thin, a miniaturization is easy. Furthermore, if a low-specific-gravity metallic material like aluminum is used, a fuel cell can be lightweight-ized further. However, in a metal separator, there is a problem of being easy to corrode the metal of a base material itself. It is reported that especially an aluminum base material has a dramatically large corrosion rate (R.L.Rorup, et al., Mater.Res.Soc.Symp.Proc., 393 (1995), etc.). Moreover, when the metal ion generated by corrosion advances into an electrolyte membrane, there is a possibility of membranous ion conductivity falling and affecting the engine performance of a cell.

[0007] JP,11-162478,A is indicating the technique of improving corrosion resistance by plating noble metals on all the front faces of a metal separator. Although this technique is satisfactory about the separator engine performance, it causes high cost-ization and is not practical. Although it is necessary to make a noble-metals deposit thin for cost reduction, if thickness is made thin in the case of wet plating, a detailed pinhole will occur and it will become the cause of corrosion, and in dry type plating, productive efficiency will be bad (vacuum evaporationo, spatter, etc.), and the homogeneity of a coat will also get worse.

[0008]

[Problem(s) to be Solved by the Invention] Therefore, the object of this invention is offering the separator for the fuel cells made from aluminum which has the outstanding corrosion resistance.

[0009]

[Means for Solving the Problem] In view of the above-mentioned technical problem, wholeheartedly, as a result of research, the separator for the fuel cells made from aluminum with which this invention persons prepared the alumite coat in the part discovered that the outstanding corrosion resistance was shown, and hit on an idea of it to this invention.

[0010] That is, the separator for fuel cells of this invention consists of an aluminum metal plate, and it has the contact surface and a reactant gas aeration slot with an electrode or a charge collector, and is characterized by forming the alumite coat in the front face of this reactant gas aeration slot.

[0011] Moreover, the separator of this invention shows the further excellent corrosion resistance by filling following condition (1) - (8).

(1) It is desirable to form a conductive film in the contact surface with an electrode or a charge collector.

- (2) As for a conductive film, it is desirable to consist of the metal chosen from the group which consists of Pt, Au, Pd, Ru, Rh, Ir, and Ag or its alloy, carbon, or conductive carbide.
- (3) As for the porosity of an alumite coat, it is desirable that it is 5% or less.
- (4) As for the thickness of an alumite coat, it is desirable that it is 5-50 micrometers.
- (5) As for an alumite coat, it is desirable to be constituted by the porosity alumite coat of 10% or more of porosity formed the substantia-compacta alumite coat of 5% or less of porosity and on it.
- (6) As for the corner which reactant gas aeration Mizouchi's wall surfaces make, it is desirable to have the shape of a curved surface which has the radius of curvature of 0.5mm or more.
- (7) As for the corner which the side face and the above-mentioned contact surface of a reactant gas aeration slot make, it is desirable to have the shape of a curved surface which has the radius of curvature of 0.3mm or more.
- (8) As for the purity of an aluminum metal plate, it is desirable that it is 99.5% or more.

[0012]

[Embodiment of the Invention] The separator for fuel cells of this invention consists of an aluminum metal plate, and the alumite coat is formed in the part. By using an aluminum metal as a base material, lightweight-izing of a separator and improvement in electrical conductivity and the earthquake-proof engine performance can be aimed at. The separator of this invention can be used for various fuel cells, and can be used especially suitable for the mounted fuel cell for power of an automobile. Hereafter, although the separator of this invention is explained in full detail using drawing 1 -4, this invention is not limited to them, but unless the meaning of this invention is changed, it can add various modification.

[0013] Drawing 1 is the partial schematic diagram showing an example of the fuel cell containing the separator for fuel cells by one example of this invention. The fuel cell of drawing 1 carries out the laminating of the cell 1 which consists of the anode 3 and cathode 4 which were formed in a solid electrolyte 2 and its both sides through a separator 5, and is constituted. The ends of a laminating are connected to an external circuit (not shown).

[0014] The separator of this invention has the contact surface with an electrode or a charge collector. The configuration of this contact surface is not limited by drawing 1 that what is necessary is just the configuration where it was suitable in order to contact the electrode of a fuel cell or the carbon paper of a primary charge collector, a carbon cross, etc.

[0015] As shown in drawing 1 , the separator 5 of this invention has the reactant gas aeration slots 8 and 9. Fuel gas is supplied to the reactant gas aeration slot 9 and the path formed with an anode 3, and oxidant gas is supplied to the reactant gas aeration slot 8 and the path formed by the cathode 4. What is necessary is just to form the reactant gas aeration slots 8 and 9 in a predetermined pattern by approaches, such as machining, a press, precision casting, chemical polishing (etching), and electrolytic polishing. Although the configuration of a reactant gas aeration slot was made horseshoe-shaped by drawing 1 , especially if it is a configuration which can form the path for reactant gas in the part which touches an electrode, it will not, be limited, but it is small, and it is desirable to set up so that generation efficiency may become high. [of reactant gas ventilation resistance] Usually, as for each reactant gas aeration tooth depth, it is desirable to be referred to as 0.2-2mm, and, as for width of face, it is desirable to be referred to as 0.5-5mm.

[0016] In this invention, in order to secure the corrosion resistance of a separator, the stable alumite coat 6 is formed in the front face of the above-mentioned reactant gas aeration slot which does not contact an electrode etc. chemically and physically. An alumite coat should just form a gamma-alumina coat in a base material front face by being able to form with an anode oxidation

method etc., for example, electrolyzing, using water solutions, such as oxalic acid, a sulfuric acid, and a chromic acid, as the electrolytic solution.

[0017] By choosing anodic oxidation conditions suitably, a precise hard-anodic-oxidation-coatings coat can be formed, and it is possible to aim at much more corrosion-resistant improvement. Moreover, if it processes with a boiling water or a steam after performing anodizing, micropore peculiar to an alumite coat can be closed and corrosion resistance can be improved further. As for the porosity of an alumite coat, considering as 5% or less is desirable. Moreover, as for the thickness of an alumite coat, it is desirable to be referred to as 5-50 micrometers, and it is more desirable to be referred to as 10-30 micrometers.

[0018] It is also possible to form detailed vertical pore and a spongy porous layer in an alumite coat. As this invention shows to drawing 2, it is desirable from a viewpoint of corrosion-resistant prolonged maintenance to constitute the alumite coat 6 of a separator 5 from a porosity alumite coat 10 formed the substantia-compacta alumite coat 11 and on it. As for the porosity of this substantia-compacta alumite coat, considering as 5% or less is desirable, and, as for the porosity of a porosity alumite coat, considering as 10% or more is desirable. In this case, as for the thickness of a substantia-compacta alumite coat, it is desirable to be referred to as 2-30 micrometers, and, as for the thickness of a porosity alumite coat, it is desirable to be referred to as 5-50 micrometers. Although it is thought that the cause of corrosion-resistant degradation of an alumite coat is the crack and exfoliation which are generated when a coat carries out swelling growth in a steam and produces film distortion, film distortion can be eased by forming the above porosity alumite coats.

[0019] If there are many impurities in an aluminum base material, the homogeneity of an alumite coat will get worse and a consistency will become low. Furthermore, in such a case, once a coat is formed, the effectiveness of eburnation processing using a boiling water, a steam, etc. will become small. Therefore, as for the purity of the aluminum metal used for the separator of this invention, it is desirable that it is 99.5% or more, and it is more desirable that it is 99.9% or more. Moreover, although especially the thickness of an aluminum base material is not limited, when using for the fuel cell for mount, it is desirable to be referred to as 0.5-3mm.

[0020] In this invention, as shown in drawing 1, it is desirable to form a conductive film 7 in the contact surface (electric conduction side) with an electrode or a charge collector. That is, all the front faces of the separator of this invention have that desirable of a wrap by the non-conductive alumite coat and the conductive film.

[0021] As for a conductive film, it is desirable to form using the ingredient which has the good corrosion resistance of electrical conductivity, and it is more desirable to form with the metal chosen from the group which consists of Pt, Au, Pd, Ru, Rh, Ir, and Ag or its alloy, carbon, or conductive carbide. Contact resistance of corrosion resistance is [noble-metals system coats, such as Au, Ag, Pt, and Pd,] very good low. As carbon, the graphite film by CVD, the DLC film (diamond-like carbon film), etc. are desirable. Moreover, what added water repellent may be applied to graphite powder. Contact concordance is good when an electrode becomes carbon black from what added Pt of a minute amount, and a carbon coat is used. As conductive carbide, silicon carbide, carbonization niobium, tungsten carbide, etc. are desirable. Since it contact resistance is not only small, but has good corrosion resistance and good oxidation resistance, a carbide coat acts also as a protective coat of a separator.

[0022] A conductive film can be formed by approaches, such as a spatter, electroplating, wet plating, and CVD. Moreover, as for the thickness of a conductive film, it is desirable to be referred to as 0.01-5 micrometers. If thickness is smaller than 0.01 micrometers, film

reinforcement is weakly unstable, and since cost will become high if larger than 5 micrometers, it is not desirable.

[0023] In case a separator is incorporated into a fuel cell, in order to raise airtightness and the contact nature of a current carrying part generally, it binds tight along the direction of a stack. At this time, the planar pressure force becomes about 1-10kg/cm². Moreover, the operating temperature of a fuel cell is usually about 80-120 degrees C, and thermal expansion deformation of the separator by the temperature change takes place in many cases. On the alumite coat of the part which tends to require stress, it is easy to generate a crack and breakage, and, thereby, corrosion resistance may fall substantially. Therefore, in order to ease stress in this invention, as for the corner (R shows among drawing 3) which reactant gas aeration Mizouchi's wall surfaces make, considering as the shape of a curved surface is desirable. As for the radius of curvature of this curved surface, it is desirable to be referred to as 0.5mm or more, and it is more desirable to be referred to as 1.0mm or more.

[0024] It is easy to concentrate stress on the boundary section of the above-mentioned alumite coat and a conductive film. Moreover, in case two kinds of this coat is formed, in order for a coat to grow perpendicularly to a base material front face and not to grow up to be a longitudinal direction, it is very easy to damage the alumite coat of the above-mentioned boundary section. Therefore, as for the corner (R shows among drawing 4) which the internal side face and the above-mentioned contact surface of a gas aeration slot make in this invention, considering as the shape of a curved surface is desirable. As for the radius of curvature of this curved surface, it is desirable to be referred to as 0.3mm or more, and it is more desirable to be referred to as 0.5mm or more. Moreover, it is thought that the effectiveness which eases the film distortion originating in swelling growth of the above-mentioned alumite coat by doing in this way is also acquired.

[0025]

[Example] Hereafter, although an example explains this invention to a detail more, this invention is not limited to them.

[0026] The reactant gas aeration slot with a depth [of 1.0mm] and a width of face of 3.0mm was formed in the aluminum metal plate (1mmx150mmx150mm) of 99.6% of one to example 1 and example of comparison 3 purity by press working of sheet metal, and the separator base material was produced to it. This base material was anodized in the oxalic acid water solution, and, subsequently to ebullition underwater, it was immersed for 30 minutes, and it dried and the alumite coat of 12 micrometers of thickness was formed in the base material front face. Next, in order to raise the display flatness of the electrode contact surface of a separator, wrapping polish was carried out and the electrode contact surface was washed. The alumite coat formed on the electrode contact surface of this process is removed. Then, among the pure argon gas ambient atmosphere of 5mTorr, the spatter of the Au was carried out to the electrode contact surface, having used base material temperature as 200 degrees C, the conductive film was formed, and the separator by one example of this invention was produced. In addition, the thickness of a conductive film was about 1 micrometer.

[0027] the carbon black of the 100 weight sections -- Pt paste (Pt:90 % of the weight) of 15 weight sections -- adding -- further -- the Teflon (trademark) particle (mean particle diameter: 0.2 micrometers) of 15 weight sections was added as water repellent, and the paste for electrodes was prepared. This paste for electrodes was applied to the proton conductivity solid polymer electrolyte film (Nafion), and it dried. This was inserted by the carbon cross, it put with the above-mentioned separator of two more sheets, and the fuel cell (cell) of an example 1 was produced. The bolting pressure of a separator was made into 10kg/cm².

[0028] The fuel cell of the example 1 of a comparison using the separator made from a graphite and the fuel cell of the example 2 of a comparison using the separator made from stainless steel (SUS304) were produced like the production approach of the fuel cell of the above-mentioned example 1, respectively. Moreover, the fuel cell of the example 3 of a comparison was produced like the above-mentioned example 1 except not forming an alumite coat. In addition, the conductive film which consists of Au like the above-mentioned example 1 was formed in the electrode contact surface of the separator used in the examples 2 and 3 of a comparison.

[0029] The simulation fuel gas (70% H₂ or 15%CO₂, 15%H₂O) humidified into the reactant gas aeration slot by the side of an anode was supplied to the fuel cell (single cel) of the acquired example 1 and the examples 1-3 of a comparison, air was supplied to the cathode side aeration slot as an oxidizer, and the stability of the generation-of-electrical-energy engine performance of each fuel cell was evaluated. The corrosion-proof situation of the separator after actuation is collectively shown in a table 1 for the separator base material of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0030]

[A table 1]

セパレータ基材	初期	10日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例 1 アルマイド被膜付Al	0.84	0.80	腐食なし
比較例 1 黒鉛	0.85	0.83	-
比較例 2 ステンレス (SUS304)	0.80	0.68	溝部に若干腐食あり
比較例 3 アルマイド被膜なしAl	0.82	0.59	溝部全面に腐食あり

[0031] The separator of this invention which consists of an aluminum metal plate which prepared the alumite coat shows the outstanding corrosion resistance, and a table 1 shows that the fuel cell of an example 1 using this separator shows high generation-of-electrical-energy engine-performance stability.

[0032] The fuel cell of Examples 2a-2r and the example 4 of a comparison was produced like the above-mentioned example 1, respectively except having used each ingredient shown in a table 2 as an ingredient of example 2 and example of comparison 4 conductive film. However, when forming the conductive film of carbon (example 2q) and conductive carbide SiC (example 2r), Ar (30mTorr) was used as sputtering gas using the target of a coat presentation. The simulation fuel gas (70% H₂ or 20%CO₂, 10%H₂O) humidified in the reactant gas aeration slot by the side of an anode to the fuel cell (single cel) of the examples 1 and 4 of a comparison was supplied to obtained example 2a - 2r list, air was supplied to the cathode side aeration slot as an oxidizer, and the stability of the generation-of-electrical-energy engine performance of each fuel cell was evaluated. The corrosion-proof situation of the separator after actuation is collectively shown in a table 2 for the ingredient of the conductive film of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0033]

[A table 2]

導電性被膜	初期 (V)	10日後の (V)		耐腐食状況
		発電電圧	発電電圧	
実施例2a	Pt	0.78	0.77	腐食なし
実施例2b	Au	0.82	0.81	腐食なし
実施例2c	Pd	0.77	0.75	腐食なし
実施例2d	Ru	0.71	0.69	腐食なし
実施例2e	Rh	0.75	0.71	腐食なし
実施例2f	Ir	0.79	0.78	腐食なし
実施例2g	Ag	0.77	0.71	腐食なし
実施例2h	Pt-Au(10wt%)	0.78	0.77	腐食なし
実施例2i	Pt-Pd(10wt%)	0.78	0.74	腐食なし
実施例2j	Pt-Ru(5wt%)	0.76	0.73	腐食なし
実施例2k	Pt-Rh(5wt%)	0.75	0.72	腐食なし
実施例2l	Pt-Ir(30wt%)	0.79	0.75	腐食なし
実施例2m	Au-Pd(30wt%)	0.75	0.74	腐食なし
実施例2n	Au-Ir(30wt%)	0.69	0.66	腐食なし
実施例2o	Au-Ag(50wt%)	0.74	0.71	腐食なし
実施例2p	Pd-Ag(50wt%)	0.76	0.70	腐食なし
実施例2q	カーボン	0.82	0.81	腐食なし
実施例2r	SiC	0.84	0.83	腐食なし
比較例 1	黒鉛	0.84	0.83	—
比較例 4	Al	0.47	0.21	全面に腐食あり

[0034] The separator made from aluminum of this invention which has the desirable conductive film mentioned above shows the outstanding corrosion resistance, and a table 2 shows that the fuel cell of Examples 2a-2r using this separator shows high generation-of-electrical-energy engine-performance stability.

[0035] The fuel cell of Examples 3a-3j was produced like the above-mentioned example 1, respectively except having changed, as the porosity of an example 3 alumite coat was shown in a table 3 by changing formation conditions. The stability of the generation-of-electrical-energy engine performance of the fuel cell (single cel) of the acquired examples 3a-3j was similarly estimated as the above-mentioned example 2. The corrosion-proof situation of the separator after actuation is collectively shown in a table 3 for the porosity of the alumite coat of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0036]

[A table 3]

アルマイト被膜の 多孔度 (%)	初期 発電電圧 (V)	10日後の 発電電圧 (V)	耐腐食状況
実施例3a	0.86	0.81	良好
実施例3b	1.25	0.82	良好
実施例3c	1.63	0.86	良好
実施例3d	2.01	0.83	良好
実施例3e	2.67	0.79	ほぼ良好
実施例3f	3.02	0.84	ほぼ良好
実施例3g	3.54	0.85	ほぼ良好
実施例3h	5.06	0.88	ほぼ良好
実施例3i	7.32	0.81	腐食あり
実施例3j	10.55	0.86	腐食あり

[0037] From a table 3, the porosity of the alumite coat which the separator of this invention has is understood that it is desirable that it is 5.06% or less, and it is more desirable that it is 2.01% or less.

[0038] The fuel cell of Examples 4a-4j was produced like the above-mentioned example 1, respectively except having changed, as the thickness of an example 4 alumite coat was shown in a table 4 by adjusting film formation time amount. In addition, the porosity of an alumite coat was made into about 1.25%. The stability of the generation-of-electrical-energy engine performance of the fuel cell (single cel) of the acquired examples 4a-4j was similarly estimated as the above-mentioned example 2. The corrosion-proof situation of the separator after actuation is collectively shown in a table 4 for the thickness of the alumite coat of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0039]

[A table 4]

アルマイト被膜の 膜厚 (μm)	初期	10日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例4a	3.5	0.86	腐食あり
実施例4b	4.8	0.83	ほぼ良好
実施例4c	9.7	0.82	良好
実施例4d	15.8	0.85	良好
実施例4e	26.7	0.88	良好
実施例4f	33.1	0.81	良好
実施例4g	51.5	0.81	ほぼ良好
実施例4h	69.1	0.85	腐食あり
実施例4i	78.3	0.88	腐食あり
実施例4j	94.6	0.86	腐食あり

[0040] It turns out that it is desirable that it is 4.8-51.5 micrometers as for the thickness of the alumite coat which the separator of this invention has, and it is more more desirable than a table 4 that it is 9.7-33.1 micrometers.

[0041] By changing an electrolytic condition during formation of an example 5 alumite coat, membranous porosity was changed from the middle and the Examples [5a-5g] fuel cell was produced like the above-mentioned example 1, respectively except having formed the porosity alumite coat (thickness: about 10-30 micrometers) which has the porosity shown in a table 5 on the substantia-compacta alumite coat. In addition, the thickness of a substantia-compacta alumite coat set to about 15 micrometers, and porosity was made into 1.25%. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 5a-5g] fuel cell (single cel) was similarly estimated as the above-mentioned example 2. However, assessment was performed for 36 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 5 for the porosity of the porosity alumite coat of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during 36 days, and 36 days.

[0042]

[A table 5]

多孔質アルマイト 被膜の多孔度 (%)	初期	36日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例5a	5.6	0.79	腐食あり
実施例5b	9.4	0.82	ほぼ良好
実施例5c	19.4	0.86	良好
実施例5d	26.1	0.85	良好
実施例5e	36.7	0.84	良好
実施例5f	39.4	0.80	良好
実施例5g	46.2	0.83	良好

[0043] From a table 5, when a substantia-compacta alumite coat and a porosity alumite coat constitute the alumite coat of the separator of this invention, the porosity of a porosity alumite coat is understood that it is desirable that it is 9.4% or more, and it is more desirable that it is 19.4% or more. Moreover, in the alumite coat with which corrosion was seen, it checked that the corrosion section existed on the outskirts of a crack of a coat.

[0044] The Examples [6a-6g] fuel cell was produced like the above-mentioned example 1, respectively except having considered as the shape of a curved surface which has the radius of curvature which shows the corner which example 6 reactant-gas aeration Mizouchi's wall surfaces make in a table 6. In addition, thickness of an alumite coat was set to about 15 micrometers, and porosity was made into 1.25%. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 6a-6g] fuel cell (single cel) was similarly estimated as the above-mentioned example 2. However, assessment was performed for 34 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 6 for the above-mentioned radius of curvature of each fuel cell, and 34 days.

[0045]

[A table 6]

	曲率半径 (mm)	耐腐食状況
実施例6a	0.1	腐食あり
実施例6b	0.2	腐食あり
実施例6c	0.3	腐食あり
実施例6d	0.5	ほぼ良好
実施例6e	0.7	ほぼ良好
実施例6f	1.0	良好
実施例6g	1.5	良好

[0046] From a table 6, the above-mentioned radius of curvature of the separator of this invention is understood that it is desirable that it is 0.5mm or more, and it is more desirable that it is 1.0mm or more. Moreover, in the alumite coat with which corrosion was seen, it checked that the corrosion section existed on the outskirts of a crack of the coat in the acute-angle processing section.

[0047] The Examples [7a-7g] fuel cell was produced like the above-mentioned example 1, respectively except having considered as the shape of a curved surface which has the radius of curvature which shows the corner which the side face and the electrode contact surface of an example 7 reactant-gas aeration slot make in a table 7. In addition, the corner which reactant gas aeration Mizouchi's wall surfaces make considered as the shape of a curved surface, and the radius of curvature of the curved surface was fixed to 1.0mm. Moreover, thickness of an alumite coat was set to about 15 micrometers, and porosity was made into 1.25%. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 7a-7g] fuel cell (single cel) was similarly estimated as the above-mentioned example 2. However, assessment was performed for 34 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 7 for the radius of curvature of the corner curved surface which the side face and the electrode contact surface of a reactant gas aeration slot of

each fuel cell make, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference of 34 days after, and 34 days.

[0048]

[A table 7]

曲率半径 (mm)	初期		34日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)		
実施例7a	0.1	0.80	0.67	腐食あり
実施例7b	0.2	0.81	0.72	腐食あり
実施例7c	0.3	0.80	0.78	ほぼ良好
実施例7d	0.5	0.78	0.70	良好
実施例7e	0.7	0.83	0.81	良好
実施例7f	1.0	0.80	0.78	良好
実施例7g	1.5	0.82	0.79	良好

[0049] From a table 7, the above-mentioned radius of curvature of the separator of this invention is understood that it is desirable that it is 0.3mm or more, and it is more desirable that it is 0.5mm or more. Moreover, in the alumite coat with which corrosion was seen, it checked that the corrosion section existed on the outskirts of a crack of the coat in the acute-angle processing section.

[0050] The Examples [8a-8f] fuel cell was produced like the above-mentioned example 1, respectively except having changed the purity of an example 8 aluminum base material, as shown in a table 8. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 8a-8f] fuel cell (single cel) was similarly estimated as the above-mentioned example 1. However, assessment was performed for 12 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 8 for the purity of the aluminum base material of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference of 12 days after, and 12 days.

[0051]

[A table 8]

アルミニウム基材の 純度 (%)	初期		12日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)		
実施例8a	99.23	0.78	0.63	腐食あり
実施例8b	99.50	0.81	0.74	ほぼ良好
実施例8c	99.76	0.79	0.74	ほぼ良好
実施例8d	99.90	0.78	0.77	良好
実施例8e	99.97	0.83	0.81	良好
実施例8f	99.99	0.85	0.83	良好

[0052] From a table 8, the purity of the aluminum base material used for the separator of this

invention is understood that it is desirable that it is 99.50% or more, and it is more desirable that it is 99.90% or more.

[0053]

[Effect of the Invention] As explained in full detail above, the separator for fuel cells of this invention is dramatically lightweight in order to use aluminum as a principal component, and mass production nature can reduce processing cost highly compared with the conventional separator made from a graphite. Furthermore, in this invention, the separator made from aluminum which shows the outstanding corrosion resistance can be obtained by forming an alumite coat suitably on a base material. The fuel cell using the separator of this invention has high generation-of-electrical-energy engine-performance stability.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the separator used for a fuel cell, especially the mounted fuel cell for power of an automobile.

PRIOR ART

[Description of the Prior Art] The energy conversion efficiency of a fuel cell from a fuel to the electrical and electric equipment is high, and it attracts attention as a next-generation power plant in order not to discharge harmful matter. Especially the macromolecule ion-exchange-membrane mold fuel cell that operates in a temperature field 150 degrees C or less is studied briskly, and utilization several years after is expected. This fuel cell can operate at comparatively low temperature, its output density of a generation of electrical energy is high, and since it can miniaturize, it is suitable as a fuel cell home use and for mount.

[0003] Usually, a macromolecule ion-exchange-membrane mold fuel cell fixes a fuel electrode and an oxygen electrode (air electrode) to both sides of a solid-electrolyte membrane, forms a cell (cel), and is constituted by carrying out a laminating through the tabular separator which prepared the aeration slot which supplies fuel gas and air for this. The fluororesin system ion exchange membrane which has a sulfonic group as a solid-electrolyte membrane is used, and an electrode is formed by what distributed Repellent PTFE and the noble-metals particle catalyst to carbon black. In case a hydrogen-oxygen fuel cell operates, the proton which hydrogen gas oxidized and was produced advances into an electrolyte, combines with a water molecule, becomes H_3O^+ , and moves to a positive-electrode side. In a positive-electrode side, the oxygen introduced from the aeration slot obtains the electron generated by oxidation reaction of hydrogen, combines with the proton in an electrolyte, and serves as water. Electrical energy can be continuously taken out by continuing these reaction processes. Although the theoretical electromotive force of this cell is 1.2V, it is the causes, such as a voltage drop by the contact resistance of polarization of an electrode, the crossover (phenomenon in which fuel gas penetrates an electrolyte and leaks to an air electrode) of reactant gas, an electrode, and a charge collector, actually, and output voltage is about 0.6-0.8V. Therefore, in order to obtain a practical output, it is necessary to carry out the stack of dozens of cells through a separator, and to connect in serial.

[0004] Since H^+ exists so much in an electrolyte so that the above-mentioned generation-of-electrical-energy principle may show, water or a steam serves as [near / which exist so much / the interior of an electrolyte, and near the electrode] strong acid nature. Moreover, although

oxygen combines with H⁺ by the positive-electrode side and water is generated, a hydrogen peroxide may generate depending on the operating state of a cell. Since a separator is built into the bottom of such an environment, in addition to electrical conductivity and airtightness, it is required that it should have high chemistry and electrochemical stability (corrosion resistance). [0005] Many of conventional separators for fuel cells machine a graphite plate. Mechanical strength is low and a graphite separator has high processing cost, while electric resistance is low and corrosion resistance is high. It is difficult to apply the present graphite separator to the fuel cell for mount as it is, since for the separator used for the fuel cell for mount to have high mechanical strength, and to be able to process it by low cost is demanded. Although the method of manufacturing a separator by mixing with resin, injection molding graphite powder, and carrying out elevated-temperature baking further in recent years is examined, since the consistency of the baking object acquired is low, there is a problem that airtightness is bad. A production process becomes complicated although it is possible to raise a consistency by being immersed and carbonization re-calcinating this separator by resin. In addition, the contact electricity resistance of the separator manufactured in this way is several times as strong as the conventional graphite separator, and output voltage lowering of a cell is not avoided.

[0006] The separator which consists of a metal in addition to a graphite separator is also examined. Bulk electric resistance is low, a metal separator has high airtightness and high mechanical strength, and reduction of processing cost is easy for it. Moreover, since thickness of a separator can be made thin, a miniaturization is easy. Furthermore, if a low-specific-gravity metallic material like aluminum is used, a fuel cell can be lightweight-ized further. However, in a metal separator, there is a problem of being easy to corrode the metal of a base material itself. It is reported that especially an aluminum base material has a dramatically large corrosion rate (R.L.Rorup, et al., Mater.Res.Soc.Symp.Proc., 393 (1995), etc.). Moreover, when the metal ion generated by corrosion advances into an electrolyte membrane, there is a possibility of membranous ion conductivity falling and affecting the engine performance of a cell.

[0007] JP,11-162478,A is indicating the technique of improving corrosion resistance by plating noble metals on all the front faces of a metal separator. Although this technique is satisfactory about the separator engine performance, it causes high cost-ization and is not practical. Although it is necessary to make a noble-metals deposit thin for cost reduction, if thickness is made thin in the case of wet plating, a detailed pinhole will occur and it will become the cause of corrosion, and in dry type plating, productive efficiency will be bad (vacuum evaporationo, spatter, etc.), and the homogeneity of a coat will also get worse.

EFFECT OF THE INVENTION

[Effect of the Invention] As explained in full detail above, the separator for fuel cells of this invention is dramatically lightweight in order to use aluminum as a principal component, and mass production nature can reduce processing cost highly compared with the conventional separator made from a graphite. Furthermore, in this invention, the separator made from aluminum which shows the outstanding corrosion resistance can be obtained by forming an alumite coat suitably on a base material. The fuel cell using the separator of this invention has high generation-of-electrical-energy engine-performance stability.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Therefore, the object of this invention is offering the separator for the fuel cells made from aluminum which has the outstanding corrosion resistance.

MEANS

[Means for Solving the Problem] In view of the above-mentioned technical problem, wholeheartedly, as a result of research, the separator for the fuel cells made from aluminum with which this invention persons prepared the alumite coat in the part discovered that the outstanding corrosion resistance was shown, and hit on an idea of it to this invention.

[0010] That is, the separator for fuel cells of this invention consists of an aluminum metal plate, and it has the contact surface and a reactant gas aeration slot with an electrode or a charge collector, and is characterized by forming the alumite coat in the front face of this reactant gas aeration slot.

[0011] Moreover, the separator of this invention shows the further excellent corrosion resistance by filling following condition (1) - (8).

(1) It is desirable to form a conductive film in the contact surface with an electrode or a charge collector.

(2) As for a conductive film, it is desirable to consist of the metal chosen from the group which consists of Pt, Au, Pd, Ru, Rh, Ir, and Ag or its alloy, carbon, or conductive carbide.

(3) As for the porosity of an alumite coat, it is desirable that it is 5% or less.

(4) As for the thickness of an alumite coat, it is desirable that it is 5-50 micrometers.

(5) As for an alumite coat, it is desirable to be constituted by the porosity alumite coat of 10% or more of porosity formed the substantia-compacta alumite coat of 5% or less of porosity and on it.

(6) As for the corner which reactant gas aeration Mizouchi's wall surfaces make, it is desirable to have the shape of a curved surface which has the radius of curvature of 0.5mm or more.

(7) As for the corner which the side face and the above-mentioned contact surface of a reactant gas aeration slot make, it is desirable to have the shape of a curved surface which has the radius of curvature of 0.3mm or more.

(8) As for the purity of an aluminum metal plate, it is desirable that it is 99.5% or more.

[0012]

[Embodiment of the Invention] The separator for fuel cells of this invention consists of an aluminum metal plate, and the alumite coat is formed in the part. By using an aluminum metal as a base material, lightweight-izing of a separator and improvement in electrical conductivity and the earthquake-proof engine performance can be aimed at. The separator of this invention can be used for various fuel cells, and can be used especially suitable for the mounted fuel cell for power of an automobile. Hereafter, although the separator of this invention is explained in full detail using drawing 1 -4, this invention is not limited to them, but unless the meaning of this invention is changed, it can add various modification.

[0013] Drawing 1 is the partial schematic diagram showing an example of the fuel cell containing the separator for fuel cells by one example of this invention. The fuel cell of drawing 1 carries out the laminating of the cell 1 which consists of the anode 3 and cathode 4 which were formed in a solid electrolyte 2 and its both sides through a separator 5, and is constituted. The ends of a laminating are connected to an external circuit (not shown).

[0014] The separator of this invention has the contact surface with an electrode or a charge collector. The configuration of this contact surface is not limited by drawing 1 that what is necessary is just the configuration where it was suitable in order to contact the electrode of a fuel

cell or the carbon paper of a primary charge collector, a carbon cross, etc.

[0015] As shown in drawing 1, the separator 5 of this invention has the reactant gas aeration slots 8 and 9. Fuel gas is supplied to the reactant gas aeration slot 9 and the path formed with an anode 3, and oxidant gas is supplied to the reactant gas aeration slot 8 and the path formed by the cathode 4. What is necessary is just to form the reactant gas aeration slots 8 and 9 in a predetermined pattern by approaches, such as machining, a press, precision casting, chemical polishing (etching), and electrolytic polishing. Although the configuration of a reactant gas aeration slot was made horseshoe-shaped by drawing 1, especially if it is a configuration which can form the path for reactant gas in the part which touches an electrode, it will not be limited, but it is small, and it is desirable to set up so that generation efficiency may become high. [of reactant gas ventilation resistance] Usually, as for each reactant gas aeration tooth depth, it is desirable to be referred to as 0.2-2mm, and, as for width of face, it is desirable to be referred to as 0.5-5mm.

[0016] In this invention, in order to secure the corrosion resistance of a separator, the stable alumite coat 6 is formed in the front face of the above-mentioned reactant gas aeration slot which does not contact an electrode etc. chemically and physically. An alumite coat should just form a gamma-alumina coat in a base material front face by being able to form with an anode oxidation method etc., for example, electrolyzing, using water solutions, such as oxalic acid, a sulfuric acid, and a chromic acid, as the electrolytic solution.

[0017] By choosing anodic oxidation conditions suitably, a precise hard-anodic-oxidation-coatings coat can be formed, and it is possible to aim at much more corrosion-resistant improvement. Moreover, if it processes with a boiling water or a steam after performing anodizing, micropore peculiar to an alumite coat can be closed and corrosion resistance can be improved further. As for the porosity of an alumite coat, considering as 5% or less is desirable. Moreover, as for the thickness of an alumite coat, it is desirable to be referred to as 5-50 micrometers, and it is more desirable to be referred to as 10-30 micrometers.

[0018] It is also possible to form detailed vertical pore and a spongy porous layer in an alumite coat. As this invention shows to drawing 2, it is desirable from a viewpoint of corrosion-resistant prolonged maintenance to constitute the alumite coat 6 of a separator 5 from a porosity alumite coat 10 formed the substantia-compacta alumite coat 11 and on it. As for the porosity of this substantia-compacta alumite coat, considering as 5% or less is desirable, and, as for the porosity of a porosity alumite coat, considering as 10% or more is desirable. In this case, as for the thickness of a substantia-compacta alumite coat, it is desirable to be referred to as 2-30 micrometers, and, as for the thickness of a porosity alumite coat, it is desirable to be referred to as 5-50 micrometers. Although it is thought that the cause of corrosion-resistant degradation of an alumite coat is the crack and exfoliation which are generated when a coat carries out swelling growth in a steam and produces film distortion, film distortion can be eased by forming the above porosity alumite coats.

[0019] If there are many impurities in an aluminum base material, the homogeneity of an alumite coat will get worse and a consistency will become low. Furthermore, in such a case, once a coat is formed, the effectiveness of eburnation processing using a boiling water, a steam, etc. will become small. Therefore, as for the purity of the aluminum metal used for the separator of this invention, it is desirable that it is 99.5% or more, and it is more desirable that it is 99.9% or more. Moreover, although especially the thickness of an aluminum base material is not limited, when using for the fuel cell for mount, it is desirable to be referred to as 0.5-3mm.

[0020] In this invention, as shown in drawing 1, it is desirable to form a conductive film 7 in the

contact surface (electric conduction side) with an electrode or a charge collector. That is, all the front faces of the separator of this invention have that desirable of a wrap by the non-conductive alumite coat and the conductive film.

[0021] As for a conductive film, it is desirable to form using the ingredient which has the good corrosion resistance of electrical conductivity, and it is more desirable to form with the metal chosen from the group which consists of Pt, Au, Pd, Ru, Rh, Ir, and Ag or its alloy, carbon, or conductive carbide. Contact resistance of corrosion resistance is [noble-metals system coats, such as Au, Ag, Pt, and Pd,] very good low. As carbon, the graphite film by CVD, the DLC film (diamond-like carbon film), etc. are desirable. Moreover, what added water repellent may be applied to graphite powder. Contact concordance is good when an electrode becomes carbon black from what added Pt of a minute amount, and a carbon coat is used. As conductive carbide, silicon carbide, carbonization niobium, tungsten carbide, etc. are desirable. Since it contact resistance is not only small, but has good corrosion resistance and good oxidation resistance, a carbide coat acts also as a protective coat of a separator.

[0022] A conductive film can be formed by approaches, such as a spatter, electroplating, wet plating, and CVD. Moreover, as for the thickness of a conductive film, it is desirable to be referred to as 0.01-5 micrometers. If thickness is smaller than 0.01 micrometers, film reinforcement is weakly unstable, and since cost will become high if larger than 5 micrometers, it is not desirable.

[0023] In case a separator is incorporated into a fuel cell, in order to raise airtightness and the contact nature of a current carrying part generally, it binds tight along the direction of a stack. At this time, the planar pressure force becomes about 1-10kg/cm². Moreover, the operating temperature of a fuel cell is usually about 80-120 degrees C, and thermal expansion deformation of the separator by the temperature change takes place in many cases. On the alumite coat of the part which tends to require stress, it is easy to generate a crack and breakage, and, thereby, corrosion resistance may fall substantially. Therefore, in order to ease stress in this invention, as for the corner (R shows among drawing 3) which reactant gas aeration Mizouchi's wall surfaces make, considering as the shape of a curved surface is desirable. As for the radius of curvature of this curved surface, it is desirable to be referred to as 0.5mm or more, and it is more desirable to be referred to as 1.0mm or more.

[0024] It is easy to concentrate stress on the boundary section of the above-mentioned alumite coat and a conductive film. Moreover, in case two kinds of this coat is formed, in order for a coat to grow perpendicularly to a base material front face and not to grow up to be a longitudinal direction, it is very easy to damage the alumite coat of the above-mentioned boundary section. Therefore, as for the corner (R shows among drawing 4) which the internal side face and the above-mentioned contact surface of a gas aeration slot make in this invention, considering as the shape of a curved surface is desirable. As for the radius of curvature of this curved surface, it is desirable to be referred to as 0.3mm or more, and it is more desirable to be referred to as 0.5mm or more. Moreover, it is thought that the effectiveness which eases the film distortion originating in swelling growth of the above-mentioned alumite coat by doing in this way is also acquired.

EXAMPLE

[Example] Hereafter, although an example explains this invention to a detail more, this invention is not limited to them.

[0026] The reactant gas aeration slot with a depth [of 1.0mm] and a width of face of 3.0mm was

formed in the aluminum metal plate (1mmx150mmx150mm) of 99.6% of one to example 1 and example of comparison 3 purity by press working of sheet metal, and the separator base material was produced to it. This base material was anodized in the oxalic acid water solution, and, subsequently to ebullition underwater, it was immersed for 30 minutes, and it dried and the alumite coat of 12 micrometers of thickness was formed in the base material front face. Next, in order to raise the display flatness of the electrode contact surface of a separator, wrapping polish was carried out and the electrode contact surface was washed. The alumite coat formed on the electrode contact surface of this process is removed. Then, among the pure argon gas ambient atmosphere of 5mTorr, the spatter of the Au was carried out to the electrode contact surface, having used base material temperature as 200 degrees C, the conductive film was formed, and the separator by one example of this invention was produced. In addition, the thickness of a conductive film was about 1 micrometer.

[0027] the carbon black of the 100 weight sections -- Pt paste (Pt:90 % of the weight) of 15 weight sections -- adding -- further -- the Teflon (trademark) particle (mean particle diameter: 0.2 micrometers) of 15 weight sections was added as water repellent, and the paste for electrodes was prepared. This paste for electrodes was applied to the proton conductivity solid polymer electrolyte film (Nafion), and it dried. This was inserted by the carbon cross, it put with the above-mentioned separator of two more sheets, and the fuel cell (cell) of an example 1 was produced. The bolting pressure of a separator was made into 10kg/cm2.

[0028] The fuel cell of the example 1 of a comparison using the separator made from a graphite and the fuel cell of the example 2 of a comparison using the separator made from stainless steel (SUS304) were produced like the production approach of the fuel cell of the above-mentioned example 1, respectively. Moreover, the fuel cell of the example 3 of a comparison was produced like the above-mentioned example 1 except not forming an alumite coat. In addition, the conductive film which consists of Au like the above-mentioned example 1 was formed in the electrode contact surface of the separator used in the examples 2 and 3 of a comparison.

[0029] The simulation fuel gas (70% H₂ or 15%CO₂, 15%H₂O) humidified into the reactant gas aeration slot by the side of an anode was supplied to the fuel cell (single cel) of the acquired example 1 and the examples 1-3 of a comparison, air was supplied to the cathode side aeration slot as an oxidizer, and the stability of the generation-of-electrical-energy engine performance of each fuel cell was evaluated. The corrosion-proof situation of the separator after actuation is collectively shown in a table 1 for the separator base material of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0030]

[A table 1]

セパレータ基材	初期		10日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)		
実施例 1 アルマイド被膜付Al	0.84	0.80		腐食なし
比較例 1 黒鉛	0.85	0.83		—
比較例 2 ステンレス (SUS304)	0.80	0.68		溝部に若干腐食あり
比較例 3 アルマイド被膜なしAl	0.82	0.59		溝部全面に腐食あり

[0031] The separator of this invention which consists of an aluminum metal plate which prepared

the alumite coat shows the outstanding corrosion resistance, and a table 1 shows that the fuel cell of an example 1 using this separator shows high generation-of-electrical-energy engine-performance stability.

[0032] The fuel cell of Examples 2a-2r and the example 4 of a comparison was produced like the above-mentioned example 1, respectively except having used each ingredient shown in a table 2 as an ingredient of example 2 and example of comparison 4 conductive film. However, when forming the conductive film of carbon (example 2q) and conductive carbide SiC (example 2r), Ar (30mTorr) was used as sputtering gas using the target of a coat presentation. The simulation fuel gas (70% H₂ or 20%CO₂, 10%H₂O) humidified in the reactant gas aeration slot by the side of an anode to the fuel cell (single cel) of the examples 1 and 4 of a comparison was supplied to obtained example 2a - 2r list, air was supplied to the cathode side aeration slot as an oxidizer, and the stability of the generation-of-electrical-energy engine performance of each fuel cell was evaluated. The corrosion-proof situation of the separator after actuation is collectively shown in a table 2 for the ingredient of the conductive film of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0033]

[A table 2]

導電性被膜	発電電圧 (V)	10日後の 発電電圧 (V)		耐腐食状況
		初期	10日後の	
実施例2a	Pt	0.78	0.77	腐食なし
実施例2b	Au	0.82	0.81	腐食なし
実施例2c	Pd	0.77	0.75	腐食なし
実施例2d	Ru	0.71	0.69	腐食なし
実施例2e	Rh	0.75	0.71	腐食なし
実施例2f	Ir	0.79	0.78	腐食なし
実施例2g	Ag	0.77	0.71	腐食なし
実施例2h	Pt-Au(10wt%)	0.78	0.77	腐食なし
実施例2i	Pt-Pd(10wt%)	0.78	0.74	腐食なし
実施例2j	Pt-Ru(5wt%)	0.76	0.73	腐食なし
実施例2k	Pt-Rh(5wt%)	0.75	0.72	腐食なし
実施例2l	Pt-Ir(30wt%)	0.79	0.75	腐食なし
実施例2m	Au-Pd(30wt%)	0.75	0.74	腐食なし
実施例2n	Au-Ir(30wt%)	0.69	0.66	腐食なし
実施例2o	Au-Ag(50wt%)	0.74	0.71	腐食なし
実施例2p	Pd-Ag(50wt%)	0.76	0.70	腐食なし
実施例2q	カーボン	0.82	0.81	腐食なし
実施例2r	SiC	0.84	0.83	腐食なし
比較例 1	黒鉛	0.84	0.83	—
比較例 4	Al	0.47	0.21	全面に腐食あり

[0034] The separator made from aluminum of this invention which has the desirable conductive film mentioned above shows the outstanding corrosion resistance, and a table 2 shows that the fuel cell of Examples 2a-2r using this separator shows high generation-of-electrical-energy engine-performance stability.

[0035] The fuel cell of Examples 3a-3j was produced like the above-mentioned example 1, respectively except having changed, as the porosity of an example 3 alumite coat was shown in a table 3 by changing formation conditions. The stability of the generation-of-electrical-energy engine performance of the fuel cell (single cel) of the acquired examples 3a-3j was similarly estimated as the above-mentioned example 2. The corrosion-proof situation of the separator after actuation is collectively shown in a table 3 for the porosity of the alumite coat of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0036]

[A table 3]

アルマイト被膜の 多孔度 (%)	初期 発電電圧 (V)	10日後の 発電電圧 (V)	耐腐食状況
実施例3a	0.86	0.81	良好
実施例3b	1.25	0.82	良好
実施例3c	1.63	0.86	良好
実施例3d	2.01	0.83	良好
実施例3e	2.67	0.79	ほぼ良好
実施例3f	3.02	0.84	ほぼ良好
実施例3g	3.54	0.85	ほぼ良好
実施例3h	5.06	0.88	ほぼ良好
実施例3i	7.32	0.81	腐食あり
実施例3j	10.55	0.86	腐食あり

[0037] From a table 3, the porosity of the alumite coat which the separator of this invention has is understood that it is desirable that it is 5.06% or less, and it is more desirable that it is 2.01% or less.

[0038] The fuel cell of Examples 4a-4j was produced like the above-mentioned example 1, respectively except having changed, as the thickness of an example 4 alumite coat was shown in a table 4 by adjusting film formation time amount. In addition, the porosity of an alumite coat was made into about 1.25%. The stability of the generation-of-electrical-energy engine performance of the fuel cell (single cel) of the acquired examples 4a-4j was similarly estimated as the above-mentioned example 2. The corrosion-proof situation of the separator after actuation is collectively shown in a table 4 for the thickness of the alumite coat of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during ten days, and ten days.

[0039]

[A table 4]

アルマイト被膜の 膜厚 (μm)	初期	10日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例4a	3.5	0.86	腐食あり
実施例4b	4.8	0.83	ほぼ良好
実施例4c	9.7	0.82	良好
実施例4d	15.8	0.85	良好
実施例4e	26.7	0.88	良好
実施例4f	33.1	0.81	良好
実施例4g	51.5	0.81	ほぼ良好
実施例4h	69.1	0.85	腐食あり
実施例4i	78.3	0.88	腐食あり
実施例4j	94.6	0.86	腐食あり

[0040] It turns out that it is desirable that it is 4.8-51.5 micrometers as for the thickness of the alumite coat which the separator of this invention has, and it is more more desirable than a table 4 that it is 9.7-33.1 micrometers.

[0041] By changing an electrolytic condition during formation of an example 5 alumite coat, membranous porosity was changed from the middle and the Examples [5a-5g] fuel cell was produced like the above-mentioned example 1, respectively except having formed the porosity alumite coat (thickness: about 10-30 micrometers) which has the porosity shown in a table 5 on the substantia-compacta alumite coat. In addition, the thickness of a substantia-compacta alumite coat set to about 15 micrometers, and porosity was made into 1.25%. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 5a-5g] fuel cell (single cel) was similarly estimated as the above-mentioned example 2. However, assessment was performed for 36 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 5 for the porosity of the porosity alumite coat of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference after the actuation during 36 days, and 36 days.

[0042]

[A table 5]

多孔質アルマイト 被膜の多孔度 (%)	初期	36日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例5a	5.6	0.79	腐食あり
実施例5b	9.4	0.82	ほぼ良好
実施例5c	19.4	0.86	良好
実施例5d	26.1	0.85	良好
実施例5e	36.7	0.84	良好
実施例5f	39.4	0.80	良好
実施例5g	46.2	0.83	良好

[0043] From a table 5, when a substantia-compacta alumite coat and a porosity alumite coat constitute the alumite coat of the separator of this invention, the porosity of a porosity alumite coat is understood that it is desirable that it is 9.4% or more, and it is more desirable that it is 19.4% or more. Moreover, in the alumite coat with which corrosion was seen, it checked that the corrosion section existed on the outskirts of a crack of a coat.

[0044] The Examples [6a-6g] fuel cell was produced like the above-mentioned example 1, respectively except having considered as the shape of a curved surface which has the radius of curvature which shows the corner which example 6 reactant-gas aeration Mizouchi's wall surfaces make in a table 6. In addition, thickness of an alumite coat was set to about 15 micrometers, and porosity was made into 1.25%. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 6a-6g] fuel cell (single cel) was similarly estimated as the above-mentioned example 2. However, assessment was performed for 34 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 6 for the above-mentioned radius of curvature of each fuel cell, and 34 days.

[0045]

[A table 6]

	曲率半径 (mm)	耐腐食状況
実施例6a	0.1	腐食あり
実施例6b	0.2	腐食あり
実施例6c	0.3	腐食あり
実施例6d	0.5	ほぼ良好
実施例6e	0.7	ほぼ良好
実施例6f	1.0	良好
実施例6g	1.5	良好

[0046] From a table 6, the above-mentioned radius of curvature of the separator of this invention is understood that it is desirable that it is 0.5mm or more, and it is more desirable that it is 1.0mm or more. Moreover, in the alumite coat with which corrosion was seen, it checked that the corrosion section existed on the outskirts of a crack of the coat in the acute-angle processing section.

[0047] The Examples [7a-7g] fuel cell was produced like the above-mentioned example 1, respectively except having considered as the shape of a curved surface which has the radius of curvature which shows the corner which the side face and the electrode contact surface of an example 7 reactant-gas aeration slot make in a table 7. In addition, the corner which reactant gas aeration Mizouchi's wall surfaces make considered as the shape of a curved surface, and the radius of curvature of the curved surface was fixed to 1.0mm. Moreover, thickness of an alumite coat was set to about 15 micrometers, and porosity was made into 1.25%. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 7a-7g] fuel cell (single cel) was similarly estimated as the above-mentioned example 2. However, assessment was performed for 34 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 7 for the radius of curvature of the corner curved surface which the side face and the electrode contact surface of a reactant gas aeration slot of

each fuel cell make, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference of 34 days after, and 34 days.

[0048]

[A table 7]

曲率半径 (mm)	初期	34日後の	
	発電電圧 (V)	発電電圧 (V)	耐腐食状況
実施例7a	0.1	0.80	腐食あり
実施例7b	0.2	0.81	腐食あり
実施例7c	0.3	0.80	ほぼ良好
実施例7d	0.5	0.78	良好
実施例7e	0.7	0.83	良好
実施例7f	1.0	0.80	良好
実施例7g	1.5	0.82	良好

[0049] From a table 7, the above-mentioned radius of curvature of the separator of this invention is understood that it is desirable that it is 0.3mm or more, and it is more desirable that it is 0.5mm or more. Moreover, in the alumite coat with which corrosion was seen, it checked that the corrosion section existed on the outskirts of a crack of the coat in the acute-angle processing section.

[0050] The Examples [8a-8f] fuel cell was produced like the above-mentioned example 1, respectively except having changed the purity of an example 8 aluminum base material, as shown in a table 8. The stability of the generation-of-electrical-energy engine performance of an examples [which were acquired / 8a-8f] fuel cell (single cel) was similarly estimated as the above-mentioned example 1. However, assessment was performed for 12 days. The corrosion-proof situation of the separator after actuation is collectively shown in a table 8 for the purity of the aluminum base material of each fuel cell, an initial generation-of-electrical-energy electrical potential difference, the generation-of-electrical-energy electrical potential difference of 12 days after, and 12 days.

[0051]

[A table 8]

アルミニウム基材の 純度 (%)	初期	12日後の	
	発電電圧 (V)	発電電圧 (V)	耐腐食状況
実施例8a	99.23	0.78	腐食あり
実施例8b	99.50	0.81	ほぼ良好
実施例8c	99.76	0.79	ほぼ良好
実施例8d	99.90	0.78	良好
実施例8e	99.97	0.83	良好
実施例8f	99.99	0.85	良好

[0052] From a table 8, the purity of the aluminum base material used for the separator of this

invention is understood that it is desirable that it is 99.50% or more, and it is more desirable that it is 99.90% or more.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the partial schematic diagram showing an example of the fuel cell containing the separator for fuel cells by one example of this invention.

[Drawing 2] They are the schematic diagram showing the separator for fuel cells by one example of this invention, and the elements on larger scale showing the structure of the alumite coat.

[Drawing 3] It is the partial schematic diagram showing an example of the configuration of a reactant gas aeration slot of the separator for fuel cells of this invention.

[Drawing 4] It is the partial schematic diagram showing an example of the configuration of the contact surface with the reactant gas aeration slot and electrode of the separator for fuel cells of this invention, or a charge collector.

[Description of Notations]

- 1 ... Cell
- 2 ... Solid electrolyte
- 3 ... Anode
- 4 ... Cathode
- 5 ... Separator
- 6 ... Alumite coat
- 7 ... Conductive film
- 8 9 ... Reactant gas aeration slot
- 10 ... Porosity alumite coat
- 11 ... Substantia-compacta alumite coat

CLAIMS

[Claim(s)]

[Claim 1] The separator for fuel cells characterized by forming the alumite coat in the front face of said reactant gas aeration slot in the separator for fuel cells which consists of an aluminum metal plate and has the contact surface and a reactant gas aeration slot with an electrode or a charge collector.

[Claim 2] The separator for fuel cells characterized by forming the conductive film in the contact surface with said electrode or charge collector in the separator for fuel cells according to claim 1.

[Claim 3] The separator for fuel cells characterized by consisting of the metal chosen from the group which said conductive film becomes from Pt, Au, Pd, Ru, Rh, Ir, and Ag in the separator for fuel cells according to claim 2 or its alloy, carbon, or conductive carbide.

[Claim 4] The separator for fuel cells characterized by the porosity of said alumite coat being 5% or less in the separator for fuel cells according to claim 1 to 3.

[Claim 5] The separator for fuel cells characterized by the thickness of said alumite coat being 5-50 micrometers in the separator for fuel cells according to claim 1 to 4.

[Claim 6] The separator for fuel cells characterized by constituting said alumite coat in the separator for fuel cells according to claim 1 to 3 with the porosity alumite coat of 10% or more of porosity formed on the substantia-compacta alumite coat of 5% or less of porosity, and this

substantia-compacta alumite coat.

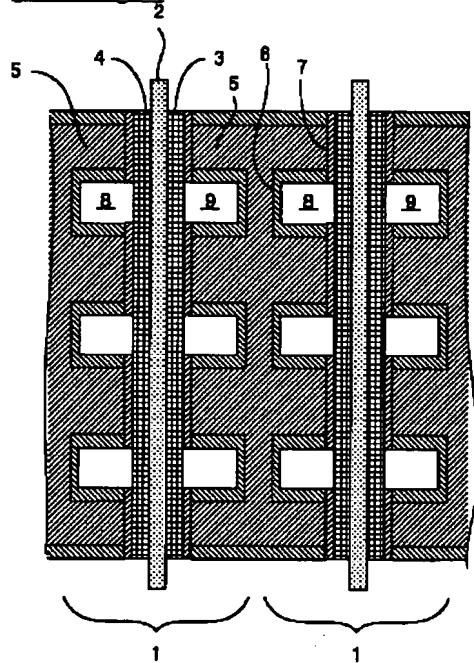
[Claim 7] The separator for fuel cells characterized by having the shape of a curved surface in which the corner which said reactant gas aeration Mizouchi's wall surfaces make has the radius of curvature of 0.5mm or more in the separator for fuel cells according to claim 1 to 6.

[Claim 8] The separator for fuel cells characterized by having the shape of a curved surface in which the corner which the side face and said contact surface of said reactant gas aeration slot make has the radius of curvature of 0.3mm or more in the separator for fuel cells according to claim 1 to 7.

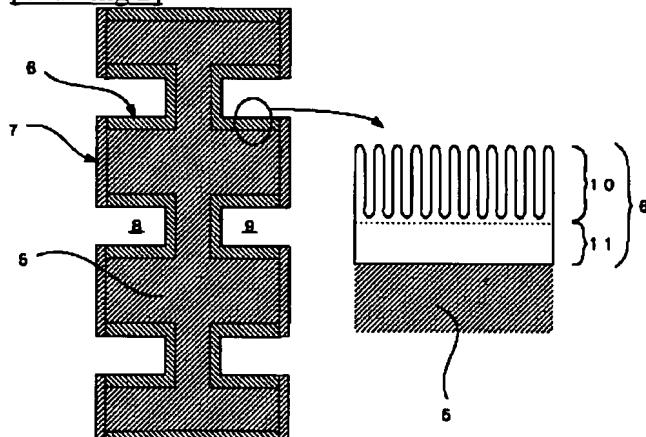
[Claim 9] The separator for fuel cells characterized by the purity of said aluminum metal plate being 99.5% or more in the separator for fuel cells according to claim 1 to 8.

DRAWINGS

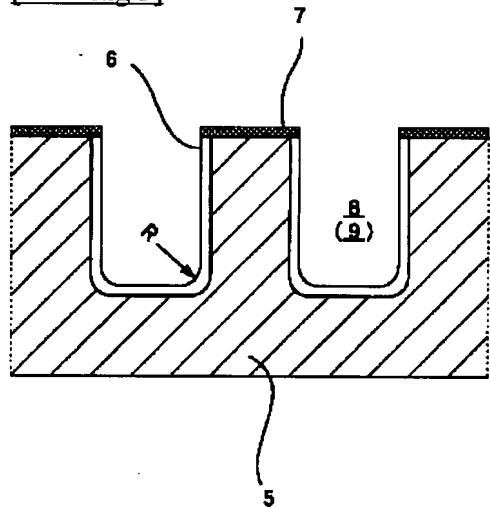
[Drawing 1]



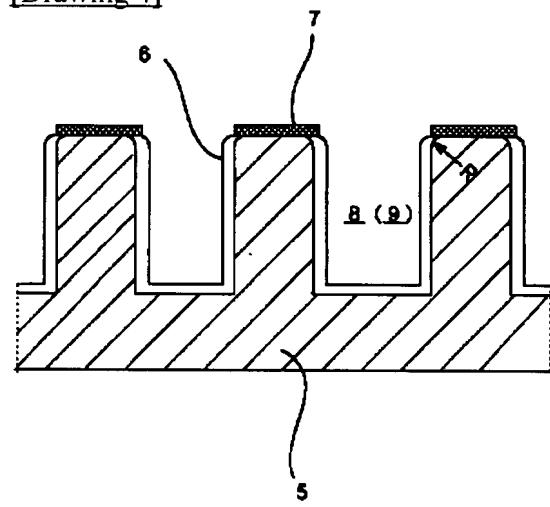
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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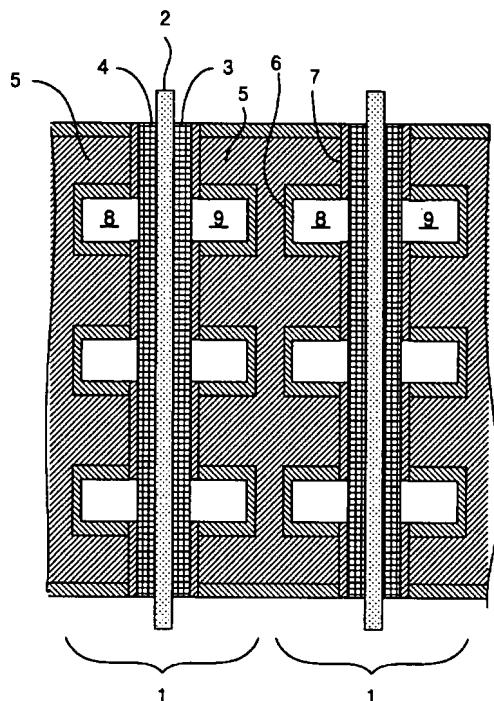
HH00 HH03 HH04 HH05

(54)【発明の名称】 燃料電池用セパレータ

(57)【要約】

【課題】 優れた耐食性を有するアルミニウム製燃料電池用セパレータを提供する。

【解決手段】 アルミニウム金属板からなり、電極又は集電体との接触面及び反応ガス通気溝を有し、該反応ガス通気溝の表面にアルマイト被膜が形成されている燃料電池用セパレータ。



【特許請求の範囲】

【請求項1】 アルミニウム金属板からなり、電極又は集電体との接触面及び反応ガス通気溝を有する燃料電池用セパレータにおいて、前記反応ガス通気溝の表面にアルマイト被膜が形成されていることを特徴とする燃料電池用セパレータ。

【請求項2】 請求項1に記載の燃料電池用セパレータにおいて、前記電極又は集電体との接触面に導電性被膜が形成されていることを特徴とする燃料電池用セパレータ。

【請求項3】 請求項2に記載の燃料電池用セパレータにおいて、前記導電性被膜がPt、Au、Pd、Ru、Rh、Ir及びAgからなる群から選ばれる金属若しくはその合金、カーボン、又は導電性炭化物からなることを特徴とする燃料電池用セパレータ。

【請求項4】 請求項1～3のいずれかに記載の燃料電池用セパレータにおいて、前記アルマイト被膜の多孔度が5%以下であることを特徴とする燃料電池用セパレータ。

【請求項5】 請求項1～4のいずれかに記載の燃料電池用セパレータにおいて、前記アルマイト被膜の膜厚が5～50μmであることを特徴とする燃料電池用セパレータ。

【請求項6】 請求項1～3のいずれかに記載の燃料電池用セパレータにおいて、前記アルマイト被膜が、多孔度5%以下の緻密質アルマイト被膜及び該緻密質アルマイト被膜上に形成される多孔度10%以上の多孔質アルマイト被膜により構成されることを特徴とする燃料電池用セパレータ。

【請求項7】 請求項1～6のいずれかに記載の燃料電池用セパレータにおいて、前記反応ガス通気溝内の壁面同士がなす角部が0.5mm以上の曲率半径を有する曲面状であることを特徴とする燃料電池用セパレータ。

【請求項8】 請求項1～7のいずれかに記載の燃料電池用セパレータにおいて、前記反応ガス通気溝の側面と前記接触面とがなす角部が0.3mm以上の曲率半径を有する曲面状であることを特徴とする燃料電池用セパレータ。

【請求項9】 請求項1～8のいずれかに記載の燃料電池用セパレータにおいて、前記アルミニウム金属板の純度が99.5%以上であることを特徴とする燃料電池用セパレータ。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は燃料電池、特に自動車の動力用車載燃料電池に用いるセパレータに関する。

【0002】

【従来の技術】 燃料電池は燃料から電気へのエネルギー変換効率が高く、有害物質を排出しないため、次世代の発電装置として注目されている。特に、150°C以下の温

度領域で作動する高分子イオン交換膜型燃料電池は盛んに研究されており、数年後の実用化が見込まれている。この燃料電池は比較的低い温度で作動でき、発電の出力密度が高く、小型化が可能であるため家庭用や車載用の燃料電池として適している。

【0003】 通常、高分子イオン交換膜型燃料電池は、固体電解質膜の両面に燃料電極及び酸素電極（空気電極）を固定して単電池（セル）を形成し、これを燃料ガスと空気を供給する通気溝を設けた板状セパレータを介して積層することにより構成される。固体電解質膜としてはスルホン酸基を有するフッ素樹脂系イオン交換膜等が用いられ、電極はカーボンブラックに撥水材PTFEと貴金属微粒子触媒を分散したもの等により形成する。水素-酸素燃料電池が作動する際には、水素ガスが酸化されて生じたプロトンが電解質中に進入し水分子と結合してH₃O⁺となり、正極側に移動する。正極側では通気溝から導入された酸素が水素の酸化反応により発生する電子を得て、電解質中のプロトンと結合し水となる。これらの反応過程を継続することにより電気エネルギーを連続的に取り出すことができる。この単電池の理論起電力は1.2Vであるが、実際には電極の分極、反応ガスのクロスオーバー（燃料ガスが電解質を透過して空気電極に漏れる現象）、電極及び集電体の接触抵抗による電圧降下等の原因で、出力電圧は0.6～0.8V程度である。従って、実用的な出力を得るために、セパレータを介して数十の単電池をスタックし直列的に接続する必要がある。

【0004】 前述の発電原理から解るように、電解質中にはH⁺が多量に存在するので、水又は水蒸気が多量に存在する電解質内部と電極の近傍では強酸性となる。また正極側で酸素がH⁺と結合して水を生成するが、電池の作動状態によっては過酸化水素が生成する場合がある。セパレータはこのような環境下に組み込まれるので、電気伝導性及び気密性に加えて、高い化学・電気化学的安定性（耐食性）を有することが要求される。

【0005】 従来の燃料電池用セパレータの多くは黒鉛板を機械加工したものである。黒鉛セパレータは電気抵抗が低く耐食性が高い反面、機械強度が低く加工コストが高い。車載用燃料電池に用いるセパレータは高い機械強度を有し低コストで加工可能であることが要求されるので、現状の黒鉛セパレータをそのまま車載用燃料電池に適用することは困難である。近年、黒鉛粉末を樹脂と混合して射出成形し、更に高温焼成することによりセパレータを製造する方法が検討されているが、得られる焼成体の密度が低いため気密性が悪いという問題がある。このセパレータを樹脂で浸漬し炭化再焼成することによって密度を高めることは可能であるが、製造工程が煩雑になる。加えて、このように製造されたセパレータの接触電気抵抗は従来の黒鉛セパレータより数倍大きく、電池の出力電圧低下が避けられない。

【0006】 黒鉛セパレータ以外に、金属からなるセパ

レータも検討されている。金属セパレータはバルク電気抵抗が低く、高い気密性及び機械強度を有し、加工コストの低減が容易である。また、セパレータの厚さを薄くできるので小型化が容易である。更に、アルミニウムのような低比重金属材料を用いると燃料電池を一層軽量化することができる。しかしながら、金属セパレータにおいては、基材の金属そのものが腐食しやすいという問題がある。特にアルミニウム基材は非常に腐食速度が大きいことが報告されている (R. L. Rorup, et al., Mater. Res. Soc. Symp. Proc., 393 (1995) 等)。また、腐食により生成した金属イオンが電解質膜に進入すると、膜のイオン伝導性が低下し電池の性能に影響を与える恐れがある。

【0007】特開平11-162478号は、貴金属を金属セパレータの全表面にメッキすることにより、耐食性を改善する手法を開示している。この手法はセパレータ性能に関しては問題が無いが、高コスト化を招き実用的ではない。コスト低減のためには貴金属メッキ層を薄くする必要があるが、湿式メッキの際に層厚を薄くすると微細なピンホールが発生し腐食の原因となり、また乾式メッキ(蒸着、スパッタ等)では生産効率が悪く、被膜の均一性も悪化してしまう。

【0008】

【発明が解決しようとする課題】従って本発明の目的は、優れた耐食性を有するアルミニウム製燃料電池用セパレータを提供することである。

【0009】

【課題を解決するための手段】上記課題に鑑み鋭意研究の結果、本発明者らは、一部にアルマイト被膜を設けたアルミニウム製燃料電池用セパレータは優れた耐食性を示すことを発見し、本発明に想到した。

【0010】すなわち、本発明の燃料電池用セパレータはアルミニウム金属板からなり、電極又は集電体との接触面及び反応ガス通気溝を有し、該反応ガス通気溝の表面にはアルマイト被膜が形成されていることを特徴とする。

【0011】また、本発明のセパレータは下記条件(1)～(8)を満たすことにより、一層優れた耐食性を示す。

- (1)電極又は集電体との接触面には導電性被膜を形成するのが好ましい。
- (2)導電性被膜はPt、Au、Pd、Ru、Rh、Ir及びAgからなる群から選ばれる金属若しくはその合金、カーボン、又は導電性炭化物からなるのが好ましい。
- (3)アルマイト被膜の多孔度は5%以下であるのが好ましい。
- (4)アルマイト被膜の膜厚は5～50μmであるのが好ましい。
- (5)アルマイト被膜は、多孔度5%以下の緻密質アルマイト被膜及びその上に形成される多孔度10%以上の多孔質アルマイト被膜により構成されるのが好ましい。

(6)反応ガス通気溝内の壁面同士がなす角部は0.5mm以上の曲率半径を有する曲面状であるのが好ましい。

(7)反応ガス通気溝の側面と上記接触面とがなす角部は0.3mm以上の曲率半径を有する曲面状であるのが好ましい。

(8)アルミニウム金属板の純度は99.5%以上であるのが好ましい。

【0012】

【発明の実施の形態】本発明の燃料電池用セパレータは

10 アルミニウム金属板からなり、その一部にはアルマイト被膜が形成されている。アルミニウム金属を基材として用いることにより、セパレータの軽量化や電気伝導性及び耐震性能の向上を図ることができる。本発明のセパレータは様々な燃料電池に使用でき、特に自動車の動力用車載燃料電池に好適に利用できる。以下、本発明のセパレータを図1～4を用いて詳述するが、本発明はそれらに限定されず、本発明の趣旨を変更しない限り種々の変更を加えることができる。

【0013】

20 図1は本発明の一実施例による燃料電池用セパレータを含む燃料電池の一例を示す部分概略図である。図1の燃料電池は、固体電解質2とその両側に設けられたアノード3及びカソード4からなる単電池1を、セパレータ5を介して積層して構成されている。積層の両端は外部回路(図示せず)に接続される。

【0014】本発明のセパレータは電極又は集電体との接触面を有する。該接触面の形状は、燃料電池の電極又は一次集電体のカーボンペーパー、カーボンクロス等と接触するために適した形状であればよく、図1により限定されない。

30 【0015】図1に示すように、本発明のセパレータ5は反応ガス通気溝8及び9を有する。反応ガス通気溝9とアノード3により形成される通路には燃料ガスが供給され、反応ガス通気溝8とカソード4により形成される通路には酸化剤ガスが供給される。反応ガス通気溝8及び9は機械加工、プレス、精密鋳造、化学研磨(エッチング)、電解研磨等の方法により所定パターンに形成すればよい。反応ガス通気溝の形状は図1ではコ字型としたが、電極に接する部分に反応ガス用通路が形成できる形状であれば特に限定されず、反応ガス通気抵抗が小さく、且つ発電効率が高くなるように設定するのが好ましい。通常、各反応ガス通気溝の深さは0.2～2mmとするのが好ましく、幅は0.5～5mmとするのが好ましい。

【0016】本発明においては、セパレータの耐食性を確保するために、電極等と接触しない上記反応ガス通気溝の表面には化学的及び物理的に安定なアルマイト被膜6を形成する。アルマイト被膜は陽極酸化法等により形成でき、例えば電解液としてシュウ酸、硫酸、クロム酸等の水溶液を用いて電解することにより、γ-アルミナ被膜を母材表面に形成すればよい。

50 【0017】陽極酸化条件を適宜選択することにより、

緻密な硬質アルマイト被膜を形成することができ、より一層の耐食性向上を図ることが可能である。また、陽極酸化処理を施した後、沸騰水又は水蒸気で処理すると、アルマイト被膜に特有な微細孔を閉じることができ耐食性を更に改善することができる。アルマイト被膜の多孔度は5%以下とするのが好ましい。また、アルマイト被膜の膜厚は5~50μmとするのが好ましく、10~30μmとするのがより好ましい。

【0018】アルマイト被膜に微細な垂直細孔や海綿状の多孔質層を形成することも可能である。本発明では、図2に示すように、セパレータ5のアルマイト被膜6を緻密質アルマイト被膜11及びその上に形成される多孔質アルマイト被膜10から構成するのが、長期間の耐食性保持の観点から好ましい。この緻密質アルマイト被膜の多孔度は5%以下とするのが好ましく、多孔質アルマイト被膜の多孔度は10%以上とするのが好ましい。この場合、緻密質アルマイト被膜の膜厚は2~30μmとするのが好ましく、多孔質アルマイト被膜の膜厚は5~50μmとするのが好ましい。アルマイト被膜の耐食性劣化の原因は、被膜が水蒸気中で膨潤成長し膜歪みを生じることにより発生するクラックや剥離であると考えられるが、前述のような多孔質アルマイト被膜を形成することにより、膜歪みを緩和することができる。

【0019】アルミニウム基材中の不純物が多いとアルマイト被膜の均一性が悪化し、密度が低くなる。更にこのような場合、被膜が一旦形成されると沸騰水、水蒸気等を用いた緻密化処理の効果が小さくなる。従って、本発明のセパレータに用いるアルミニウム金属の純度は99.5%以上であるのが好ましく、99.9%以上であるのがより好ましい。また、アルミニウム基材の厚さは特に限定されないが、車載用燃料電池に用いる場合は0.5~3mmとするのが好ましい。

【0020】本発明においては、図1に示すように、電極又は集電体との接触面（電気伝導面）には導電性被膜7を形成するのが好ましい。すなわち、本発明のセパレータの全表面は非導電性アルマイト被膜及び導電性被膜により覆うのが好ましい。

【0021】導電性被膜は電気伝導性の良い耐食性を有する材料を用いて形成するのが好ましく、Pt、Au、Pd、Ru、Rh、Ir及びAgからなる群から選ばれる金属若しくはその合金、カーボン、又は導電性炭化物により形成するのがより好ましい。Au、Ag、Pt、Pd等の貴金属系被膜は、接触抵抗が低く耐食性も極めて良好である。カーボンとしてはCVDによる黒鉛膜、DLC膜（ダイヤモンドライカーボン膜）等が好ましい。また黒鉛粉に撥水剤を添加したものを塗布しても良い。電極がカーボンブラックに微量のPtを添加したもの等からなる場合、カーボン被膜を用いると接触なじみが良い。導電性炭化物としては炭化ケイ素、炭化ニオブ、炭化タンゲステン等が好ましい。炭化物被膜は接触抵抗が小さいのみならず、良好な

耐食性及び耐酸化性を有するので、セパレータの保護膜としても作用する。

【0022】導電性被膜はスパッタ法、電気メッキ、湿式メッキ、CVD等の方法により形成できる。また導電性被膜の膜厚は0.01~5μmとするのが好ましい。膜厚が0.01μmより小さいと膜強度が弱く不安定であり、5μmより大きいとコストが高くなるため好ましくない。

【0023】セパレータを燃料電池中に組み込む際には、一般に気密性及び導電部の接触性を向上させるため

10 にスタッカ方向に沿って締め付ける。このとき面圧力は約1~10kg/cm²となる。また燃料電池の作動温度は通常約80~120°Cであり、温度変化によるセパレータの熱膨張変形が起こることが多い。応力がかかりやすい箇所のアルマイト被膜には亀裂・破損が発生しやすく、それにより耐食性が大幅に低下する場合がある。従って、本発明では応力を緩和するために反応ガス通気溝内の壁面同士がなす角部（図3中、Rで示す）は曲面状とするのが好ましい。この曲面の曲率半径は0.5mm以上とするのが好ましく、1.0mm以上とするのがより好ましい。

20 【0024】上記アルマイト被膜と導電性被膜の境界部には応力が集中しやすい。またこの二種類の被膜を形成する際には、基材表面に対して垂直方向に被膜が成長し横方向には成長しないため、上記境界部のアルマイト被膜は非常に破損しやすい。従って本発明では、ガス通気溝の内部側面と上記接触面とがなす角部（図4中、Rで示す）は曲面状とするのが好ましい。この曲面の曲率半径は0.3mm以上とするのが好ましく、0.5mm以上とするのがより好ましい。またこのようにすることで、前述のアルマイト被膜の膨潤成長に由来する膜歪みを緩和する効果も得られると考えられる。

【0025】

【実施例】以下、実施例により本発明をより詳細に説明するが、本発明はそれらに限定されるものではない。

【0026】実施例1及び比較例1~3

純度99.6%のアルミニウム金属板（1mm×150mm×150mm）に、プレス加工により深さ1.0mm及び幅3.0mmの反応ガス通気溝を形成し、セパレータ基材を作製した。この基材をショウ酸水溶液中で陽極酸化し、次いで沸騰水中に30分間浸漬し、乾燥して基材表面に膜厚12μmのアルマイト被膜を形成した。次に、セパレータの電極接触面の平坦度を向上させるために、電極接触面をラッピング研磨し、洗浄した。この工程により電極接触面上に形成されたアルマイト被膜は除去される。続いて、5mTorrの純アルゴンガス雰囲気中、基材温度を200°Cとして電極接触面にAuをスパッタして導電性被膜を形成し、本発明の一実施例によるセパレータを作製した。なお、導電性被膜の厚さは約1μmであった。

【0027】100重量部のカーボンブラックに15重量部のPtペースト（Pt:90重量%）を添加し、更に15重量部のテフロン（登録商標）粒子（平均粒径:0.2μm）を撥

水剤として添加して電極用ペーストを調製した。この電極用ペーストをプロトン伝導性高分子固体電解質膜 (Nafion) に塗布し、乾燥した。これをカーボンクロスで挟み、更に2枚の上記セパレータで挟み込んで実施例1の燃料電池（単電池）を作製した。セパレータの締め付け圧力は10kg/cm²とした。

【0028】上記実施例1の燃料電池の作製方法と同様にして、黒鉛製セパレータを用いた比較例1の燃料電池、及びステンレス (SUS304) 製セパレータを用いた比較例2の燃料電池をそれぞれ作製した。また、アルマイト被膜を形成しないこと以外は上記実施例1と同様に、比較例3の燃料電池を作製した。なお、比較例2及び3*

*で用いたセパレータの電極接触面には上記実施例1と同様にAuからなる導電性被膜を形成した。

【0029】得られた実施例1及び比較例1～3の燃料電池（単セル）に対して、アノード側の反応ガス通気溝に加湿した模擬燃料ガス (70%H₂、15%CO₂、15%H₂O) を供給し、カソード側通気溝に酸化剤として空気を供給して、各燃料電池の発電性能の安定性を評価した。各燃料電池のセパレータ基材、初期発電電圧、10日間作動後の発電電圧、及び10日間作動後のセパレータの耐腐食状況を表1に併せて示す。

【0030】

【表1】

セパレータ基材	初期 (V)	10日後の (V)		耐腐食状況
		発電電圧	発電電圧	
実施例1 アルマイト被膜付Al	0.84	0.80		腐食なし
比較例1 黒鉛	0.85	0.83		—
比較例2 ステンレス (SUS304)	0.80	0.68		溝部に若干腐食あり
比較例3 アルマイト被膜なしAl	0.82	0.59		溝部全面に腐食あり

【0031】表1より、アルマイト被膜を設けたアルミニウム金属板からなる本発明のセパレータは優れた耐食性を示し、該セパレータを用いた実施例1の燃料電池は高い発電性能安定性を示すことがわかる。

【0032】実施例2及び比較例4

導電性被膜の材料として表2に示す各材料を用いたこと以外は上記実施例1と同様に、実施例2a～2r及び比較例4の燃料電池をそれぞれ作製した。ただし、カーボン（実施例2q）及び導電性炭化物SiC（実施例2r）の導電性被膜を形成する際には、被膜組成のターゲットを用いスパッタガスとしてAr (30mTorr) を用いた。得られた

実施例2a～2r並びに比較例1及び4の燃料電池（単セル）に対して、アノード側の反応ガス通気溝に加湿した模擬燃料ガス (70%H₂、20%CO₂、10%H₂O) を供給し、カソード側通気溝に酸化剤として空気を供給して、各燃料電池の発電性能の安定性を評価した。各燃料電池の導電性被膜の材料、初期発電電圧、10日間作動後の発電電圧、及び10日間作動後のセパレータの耐腐食状況を表2に併せて示す。

30 【0033】

【表2】

導電性被膜	初期 (V)	10日後の (V)		耐腐食状況
		発電電圧	発電電圧	
実施例2a	Pt	0.78	0.77	腐食なし
実施例2b	Au	0.82	0.81	腐食なし
実施例2c	Pd	0.77	0.75	腐食なし
実施例2d	Ru	0.71	0.69	腐食なし
実施例2e	Rh	0.75	0.71	腐食なし
実施例2f	Ir	0.79	0.78	腐食なし
実施例2g	Ag	0.77	0.71	腐食なし
実施例2h	Pt-Au(10wt%)	0.78	0.77	腐食なし
実施例2i	Pt-Pd(10wt%)	0.78	0.74	腐食なし
実施例2j	Pt-Ru(5wt%)	0.76	0.73	腐食なし
実施例2k	Pt-Rh(5wt%)	0.75	0.72	腐食なし
実施例2l	Pt-Ir(30wt%)	0.79	0.75	腐食なし
実施例2m	Au-Pd(30wt%)	0.75	0.74	腐食なし
実施例2n	Au-Ir(30wt%)	0.69	0.66	腐食なし
実施例2o	Au-Ag(50wt%)	0.74	0.71	腐食なし
実施例2p	Pd-Ag(50wt%)	0.76	0.70	腐食なし
実施例2q	カーボン	0.82	0.81	腐食なし
実施例2r	SiC	0.84	0.83	腐食なし
比較例 1	黒鉛	0.84	0.83	—
比較例 4	Al	0.47	0.21	全面に腐食あり

【0034】表2より、前述した好ましい導電性被膜を有する本発明のアルミニウム製セパレータは優れた耐食性を示し、該セパレータを用いた実施例2a～2rの燃料電池は高い発電性能安定性を示すことがわかる。

【0035】実施例3

アルマイト被膜の多孔度を、形成条件を変化させることにより表3に示すように変えたこと以外は上記実施例1と同様に、実施例3a～3jの燃料電池をそれぞれ作製し

た。得られた実施例3a～3jの燃料電池（単セル）の発電性能の安定性を上記実施例2と同様に評価した。各燃料電池のアルマイト被膜の多孔度、初期発電電圧、10日間作動後の発電電圧、及び10日間作動後のセパレータの耐腐食状況を表3に併せて示す。

【0036】

【表3】

アルマイト被膜の 多孔度 (%)	初期	10日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例3a	0.86	0.81	良好
実施例3b	1.25	0.82	良好
実施例3c	1.63	0.86	良好
実施例3d	2.01	0.83	良好
実施例3e	2.67	0.79	ほぼ良好
実施例3f	3.02	0.84	ほぼ良好
実施例3g	3.54	0.85	ほぼ良好
実施例3h	5.06	0.88	ほぼ良好
実施例3i	7.32	0.81	腐食あり
実施例3j	10.55	0.86	腐食あり

【0037】表3より、本発明のセパレータが有するアルマイト被膜の多孔度は、5.06%以下であるのが好ましく、2.01%以下であるのがより好ましいことがわかる。

【0038】実施例4

アルマイト被膜の膜厚を、膜形成時間を調整することにより表4に示すように変えたこと以外は上記実施例1と同様に、実施例4a～4jの燃料電池をそれぞれ作製した。

なお、アルマイト被膜の多孔度は約1.25%とした。得ら*

*れた実施例4a～4jの燃料電池（単セル）の発電性能の安定性を上記実施例2と同様に評価した。各燃料電池のアルマイト被膜の膜厚、初期発電電圧、10日間作動後の発電電圧、及び10日間作動後のセパレータの耐腐食状況を表4に併せて示す。

【0039】

【表4】

アルマイト被膜の 膜厚 (μm)	初期	10日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例4a	3.5	0.86	腐食あり
実施例4b	4.8	0.83	ほぼ良好
実施例4c	9.7	0.82	良好
実施例4d	15.8	0.85	良好
実施例4e	26.7	0.88	良好
実施例4f	33.1	0.81	良好
実施例4g	51.5	0.81	ほぼ良好
実施例4h	69.1	0.85	腐食あり
実施例4i	78.3	0.88	腐食あり
実施例4j	94.6	0.86	腐食あり

【0040】表4より、本発明のセパレータが有するアルマイト被膜の膜厚は、4.8～51.5 μm であるのが好ましく、9.7～33.1 μm であるのがより好ましいことがわかる。

【0041】実施例5

アルマイト被膜の形成中に電解条件を変えることにより、途中から膜の多孔度を変え、緻密質アルマイト被膜上に表5に示す多孔度を有する多孔質アルマイト被膜

（膜厚：約10～30 μm ）を形成したこと以外は上記実施例1と同様に、実施例5a～5gの燃料電池をそれぞれ作製した。なお、緻密質アルマイト被膜の膜厚は約15 μm とし、多孔度は1.25%とした。得られた実施例5a～5gの燃料電池（単セル）の発電性能の安定性を上記実施例2と同様に評価した。ただし、評価は36日間行った。各燃料電池の多孔質アルマイト被膜の多孔度、初期発電電圧、

50 36日間作動後の発電電圧、及び36日間作動後のセパレー

タの耐腐食状況を表5に併せて示す。

【0042】

*【表5】

*

多孔質アルマイト 被膜の多孔度 (%)	初期 発電電圧 (V)	36日後の 発電電圧 (V)	耐腐食状況
	* 【表5】		
実施例5a	5.6	0.79	腐食あり
実施例5b	9.4	0.82	ほぼ良好
実施例5c	19.4	0.86	良好
実施例5d	26.1	0.85	良好
実施例5e	36.7	0.84	良好
実施例5f	39.4	0.80	良好
実施例5g	46.2	0.83	良好

【0043】表5より、本発明のセパレータのアルマイト被膜を緻密質アルマイト被膜及び多孔質アルマイト被膜により構成する場合、多孔質アルマイト被膜の多孔度は9.4%以上であるのが好ましく、19.4%以上であるのがより好ましいことがわかる。また、腐食が見られたアルマイト被膜においては、被膜のクラック周辺に腐食部が存在していることを確認した。

【0044】実施例6

反応ガス通気溝内の壁面同士がなす角部を、表6に示す曲率半径を有する曲面状としたこと以外は上記実施例1と同様に、実施例6a～6gの燃料電池をそれぞれ作製した。なお、アルマイト被膜の厚みは約15μmとし、多孔度は1.25%とした。得られた実施例6a～6gの燃料電池（単セル）の発電性能の安定性を上記実施例2と同様に評価した。ただし、評価は34日間行った。各燃料電池の上記曲率半径及び34日間作動後のセパレータの耐腐食状況を表6に併せて示す。

【0045】

【表6】

	曲率半径 (mm)	耐腐食状況
実施例6a	0.1	腐食あり
実施例6b	0.2	腐食あり
実施例6c	0.3	腐食あり
実施例6d	0.5	ほぼ良好
実施例6e	0.7	ほぼ良好
実施例6f	1.0	良好
実施例6g	1.5	良好

【0046】表6より、本発明のセパレータの上記曲率半径は0.5mm以上であるのが好ましく、1.0mm以上であるのがより好ましいことがわかる。また、腐食が見られたアルマイト被膜においては、鋭角加工部での被膜のクラック周辺に腐食部が存在していることを確認した。

20 【0047】実施例7

反応ガス通気溝の側面と電極接触面とがなす角部を、表7に示す曲率半径を有する曲面状としたこと以外は上記実施例1と同様に、実施例7a～7gの燃料電池をそれぞれ作製した。なお、反応ガス通気溝内の壁面同士がなす角部は曲面状とし、その曲面の曲率半径は1.0mmに固定した。また、アルマイト被膜の厚みは約15μmとし、多孔度は1.25%とした。得られた実施例7a～7gの燃料電池（単セル）の発電性能の安定性を上記実施例2と同様に評価した。ただし、評価は34日間行った。各燃料電池の上記曲率半径及び34日間作動後のセパレータの耐腐食状況を表7に併せて示す。

【0048】

【表7】

曲率半径 (mm)	初期	34日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例7a	0.1	0.80	腐食あり
実施例7b	0.2	0.81	腐食あり
実施例7c	0.3	0.80	ほぼ良好
実施例7d	0.5	0.78	良好
実施例7e	0.7	0.83	良好
実施例7f	1.0	0.80	良好
実施例7g	1.5	0.82	良好

【0049】表7より、本発明のセパレータの上記曲率半径は0.3mm以上であるのが好ましく、0.5mm以上であるのがより好ましいことがわかる。また、腐食が見られたアルマイト被膜においては、鋭角加工部での被膜のクラック周辺に腐食部が存在していることを確認した。

【0050】実施例8

アルミニウム基材の純度を表8に示すように変えたこと
以外は上記実施例1と同様に、実施例8a～8fの燃料電池*20

*をそれぞれ作製した。得られた実施例8a～8fの燃料電池（単セル）の発電性能の安定性を上記実施例1と同様に評価した。ただし、評価は12日間行った。各燃料電池のアルミニウム基材の純度、初期発電電圧、12日後の発電電圧、及び12日間作動後のセパレータの耐腐食状況を表8に併せて示す。

【0051】

【表8】

アルミニウム基材の 純度 (%)	初期	12日後の	耐腐食状況
	発電電圧 (V)	発電電圧 (V)	
実施例8a	99.23	0.78	腐食あり
実施例8b	99.50	0.81	ほぼ良好
実施例8c	99.76	0.79	ほぼ良好
実施例8d	99.90	0.78	良好
実施例8e	99.97	0.83	良好
実施例8f	99.99	0.85	良好

【0052】表8より、本発明のセパレータに用いるアルミニウム基材の純度は99.50%以上であるのが好ましく、99.90%以上であるのがより好ましいことがわかる。

【0053】

【発明の効果】以上詳述したように、本発明の燃料電池用セパレータはアルミニウムを主成分とするため非常に軽量であり、従来の黒鉛製セパレータに比べ量産性が高く加工コストを低減できる。更に本発明においては、基材上に適宜アルマイト被膜を形成することにより、優れた耐食性を示すアルミニウム製セパレータを得ることができる。本発明のセパレータを用いた燃料電池は高い発電性能安定性を有する。

【図面の簡単な説明】

【図1】 本発明の一実施例による燃料電池用セパレータを含む燃料電池の一例を示す部分概略図である。

【図2】 本発明の一実施例による燃料電池用セパレータを示す概略図、及びそのアルマイト被膜の構造を示す

部分拡大図である。

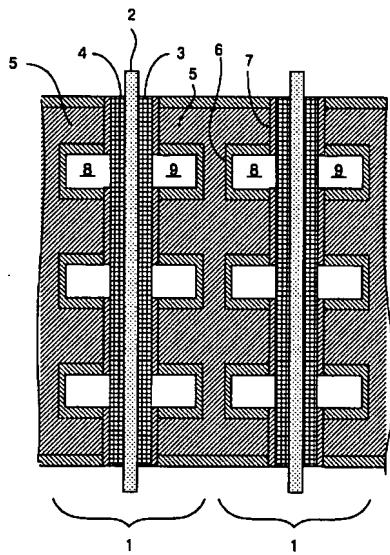
【図3】 本発明の燃料電池用セパレータの、反応ガス通気溝の形状の一例を示す部分概略図である。

【図4】 本発明の燃料電池用セパレータの、反応ガス通気溝及び電極又は集電体との接触面の形状の一例を示す部分概略図である。

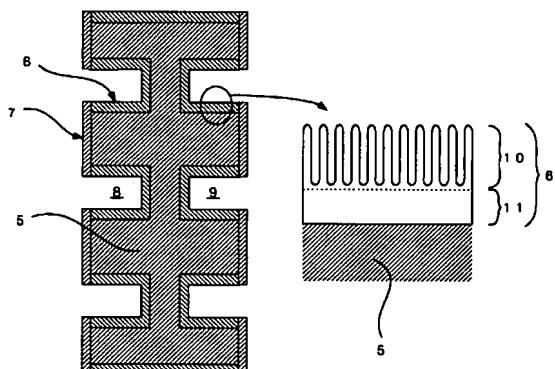
【符号の説明】

1 . . . 単電池
2 . . . 固体電解質
3 . . . アノード
4 . . . カソード
5 . . . セパレータ
6 . . . アルマイト被膜
7 . . . 導電性被膜
8、9 . . . 反応ガス通気溝
10 . . . 多孔質アルマイト被膜
11 . . . 細密質アルマイト被膜

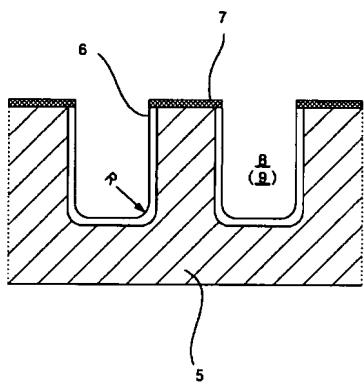
【図1】



【図2】



【図3】



【図4】

